

Chapter-16

Lesson-1

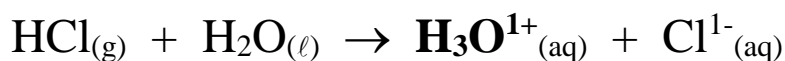
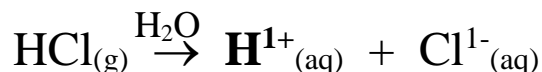
I – Arrhenius and Brønsted-Lowry Acids and Bases

A) Characteristic Properties of Acids and Bases

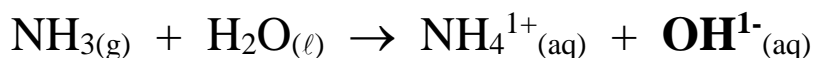
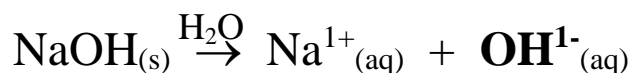
Acids...	Bases...
<i>Taste sour</i>	<i>Taste bitter</i>
<i>React w/ metals to produce $H_{2(g)}$</i>	<i>Feel slippery</i>
<i>Turn methyl orange to red</i>	<i>Turn methyl orange to yellow</i>
<i>Turn bromcresol green to yellow</i>	<i>Turn bromcresol green to blue</i>
<i>Turn litmus to red</i>	<i>Turn litmus to blue</i>
<i>Turn bromthymol blue to yellow</i>	<i>Turn bromthymol blue to blue</i>
<i>Turn thymol blue to yellow</i>	<i>Turn thymol blue to blue</i>
<i>Turn phenolphthalein to colorless</i>	<i>Turn phenolphthalein to pink</i>

B) Arrhenius Theory

- An **acid** is a substance that produces an excess of H^{1+} (H_3O^{1+}) ions in aqueous solutions.



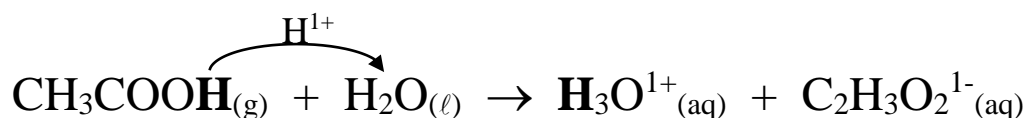
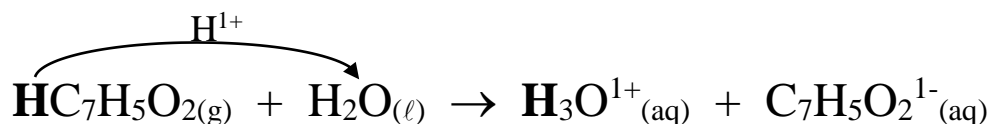
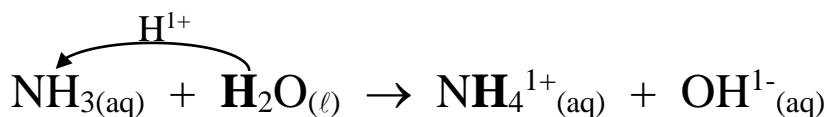
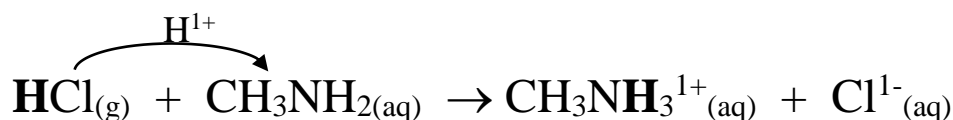
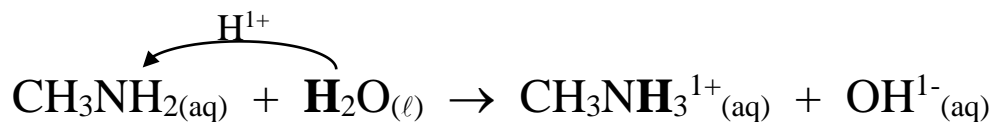
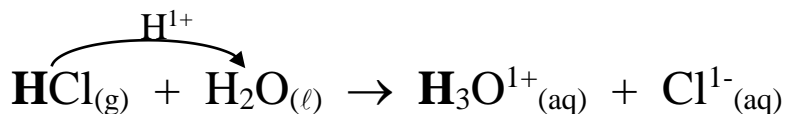
- Stronger **Arrhenius acids** produce more aqueous H^{1+} (H_3O^{1+}) ions than weaker **Arrhenius acids**.
- A **base** is a substance that produces an excess of OH^{1-} ions in aqueous solutions.



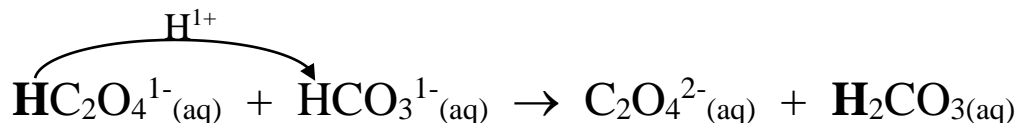
- Stronger **Arrhenius bases** produce more aqueous OH^{1-} ions than weaker **Arrhenius bases**.

C) Brønsted-Lowry Theory

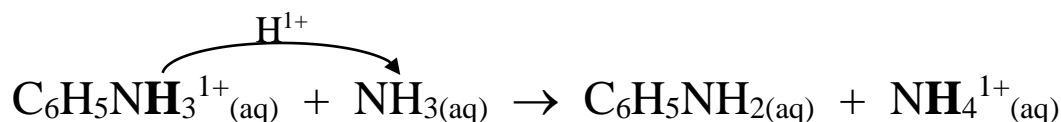
- An **acid** is a substance that donates protons (H^+) during a reaction.
- A **base** is a substance that accepts protons (H^+) during a reaction.



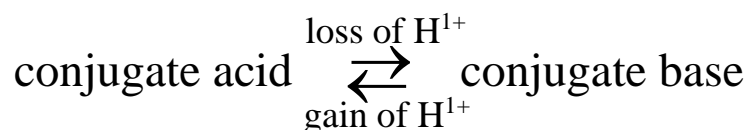
- Stronger **Bronsted-Lowry acids** are more highly ionized in water than weaker **Bronsted-Lowry acids** and thus produce more aqueous H^+ (H_3O^{1+}) ions in solution.
- Stronger **Bronsted-Lowry acids** have larger K_a values than weaker **Bronsted-Lowry acids**. (see appendix D: Table D-1)



- Stronger **Bronsted-Lowry bases** are more highly ionized in water than weaker **Bronsted-Lowry bases** and thus produce more aqueous OH^{1-} ions in solution.
- Stronger **Bronsted-Lowry bases** have larger K_b values than weaker **Bronsted-Lowry bases**. (see appendix D: Table D-2)

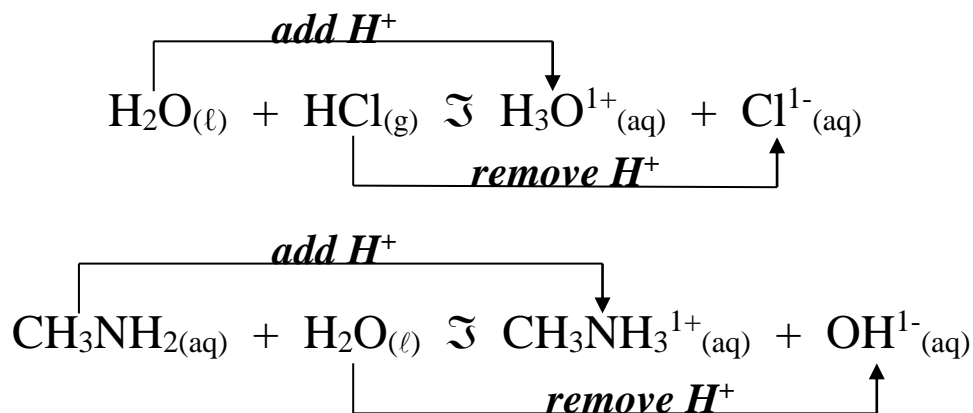


- A species formed from an acid by the loss of a proton is called the conjugate base of that acid.
- A species formed from a base by gaining a proton is called the conjugate acid of that base.



- *The stronger an acid, the weaker is its conjugate base.*
- *The stronger a base, the weaker is its conjugate acid.*
- Two species related to each other through the gain or loss of a proton are called a conjugate (acid-base) pair.

<i>Conjugate Acid-Base Pairs</i>	
<i>Conjugate Acid</i>	<i>Conjugate Base</i>
HCl	Cl ¹⁻
H ₂ S	HS ¹⁻
HS ¹⁻	S ²⁻
NH ₄ ¹⁺	NH ₃
CH ₃ NH ₃ ¹⁺	CH ₃ NH ₂



Q1: Identify the conjugate base for each of the acids and the conjugate acid for each of the bases.

Acids: HPO₄²⁻, H₂SO₄, CH₃CH₂NH₃¹⁺

Bases: S²⁻, HCO₃¹⁻, NH₃

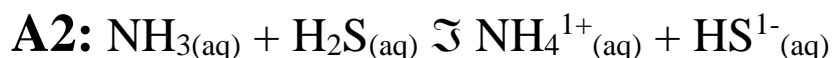
A1: Conjugate Bases: PO₄³⁻, HSO₄¹⁻, CH₃CH₂NH₂

Conjugate Acids: HS¹⁻, H₂CO₃, NH₄¹⁺

D) Brønsted-Lowry Acid-Base Reactions and Equilibrium

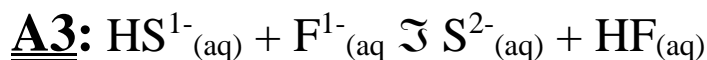
- A Bronsted-Lowry acid-base reaction is a proton-transfer reaction.
- The equilibrium of a Bronsted-Lowry acid-base reaction depends on the ability of the acid to donate a proton and the ability of the base to accept a proton:
 - ☛ Equilibrium lies to the right if a stronger acid and stronger base are reacting in the forward reaction compared to the reverse.
 - ☛ Equilibrium lies to the left if a weaker acid and weaker base are reacting in the forward reaction compared to the reverse.
- The relative strengths of some acid-base conjugate pairs are illustrated in Figure 16.4 in your textbook.

Q2: Predict the products of the Bronsted-Lowry acid-base reaction between $\text{NH}_{3(\text{aq})}$ and $\text{H}_2\text{S}_{(\text{aq})}$ and write a balanced equilibrium reaction. Also predict whether the equilibrium of the reaction lies to the left or to the right. [$K_b \text{ NH}_3 = 1.8 \times 10^{-5}$ & $K_b \text{ HS}^{1-} = 1.1 \times 10^{-7}$]



Since $\text{NH}_{3(\text{aq})}$ is a stronger base than $\text{HS}^{1-}_{(\text{aq})}$ and since $\text{H}_2\text{S}_{(\text{aq})}$ is a stronger acid than $\text{NH}_4^{1+}_{(\text{aq})}$, then the equilibrium of the reaction lies to the right.

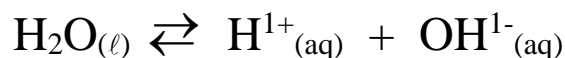
Q3: Predict the products of the Bronsted-Lowry acid-base reaction between $\text{HS}^{1-}_{(\text{aq})}$ and $\text{F}^{1-}_{(\text{aq})}$ and write a balanced equilibrium reaction. Also predict whether the equilibrium of the reaction lies to the left or to the right. [$K_a \text{ HF} = 6.8 \times 10^{-4}$ & $K_a \text{ HS}^{1-} = 1.0 \times 10^{-19}$]



Since $\text{HS}^{1-}_{(\text{aq})}$ is a weaker acid than $\text{HF}_{(\text{aq})}$ and since $\text{F}^{1-}_{(\text{aq})}$ is a weaker base than $\text{S}^{2-}_{(\text{aq})}$, then the equilibrium of the reaction lies to the left.

II – The Autoionization of Pure Water

- Pure water does ionize to a very small extent.



This process is called the **autoionization** of water.

- In pure water the $[\text{H}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7} \text{ M}$
- The equilibrium expression for the autoionization reaction is

$$K = \frac{[\text{H}^{1+}][\text{OH}^{1-}]}{[\text{H}_2\text{O}]}$$

Since the concentration of water is very large compared to the concentration of the ions and remains virtually constant at 55M, the expression is usually written as

$$K[\text{H}_2\text{O}] = [\text{H}^{1+}][\text{OH}^{1-}]$$

or

$$\mathbf{K_w = [H^{1+}][OH^{1-}]}$$

- Since in pure water the $[\text{H}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7} \text{ M}$, then

$$\mathbf{K_w = 1.0 \times 10^{-14}}$$

This equation is valid for pure water as well as for **ALL** other aqueous solutions.

- In **pure water**, $[\text{H}^{1+}] = [\text{OH}^{1-}]$, and $[\text{H}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14}$.
- In **neutral solutions**, $[\text{H}^{1+}] = [\text{OH}^{1-}]$, and $[\text{H}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14}$.
- In **acidic solutions**, $[\text{H}^{1+}] > [\text{OH}^{1-}]$, but $[\text{H}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14}$.
- In **basic solutions**, $[\text{H}^{1+}] < [\text{OH}^{1-}]$, but $[\text{H}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14}$.

Q4: In seawater, the hydrogen ion concentration is equal to $5.0 \times 10^{-9} \text{ M}$. Calculate the hydroxide ion concentration.

A4: $K_w = [\text{H}^{1+}][\text{OH}^{1-}]$

$$1.0 \times 10^{-14} = [5.0 \times 10^{-9}][X]$$

$$\boxed{X = 2.0 \times 10^{-6} \text{ M}}$$

Chapter-16

Lesson-2

III – pH and the pH Scale & pOH and the pOH Scale

- In 1909, Soren Sorensen proposed the term pH (for "power of the hydrogen ion") which equaled the negative logarithm of the hydrogen ion concentration.

$$\text{pH} = -\log [\text{H}^{1+}]$$

This allowed for a measure without the awkward negative index. As innovations go, pH and pOH was immediately embraced by the scientific community.

- A solution's pH is a measure of its acidity or alkalinity.
 - ☐ In pure water the $\text{pH} = 7.00$ $[\text{H}^{+}] = 1.0 \times 10^{-7} \text{ M}$
 - ☐ In an acidic solution $\text{pH} < 7.00$ $[\text{H}^{+}] > 1.0 \times 10^{-7} \text{ M}$
 - ☐ In a basic solution $\text{pH} > 7.00$ $[\text{H}^{+}] < 1.0 \times 10^{-7} \text{ M}$
- All aqueous solutions contain hydrogen ions $[\text{H}^{1+}]$ and thus have a pH value.

Q1: What is the pH of a solution whose $[\text{H}^{1+}] = 2.4 \times 10^{-6} \text{ M}$?

A1: $\text{pH} = -\log [\text{H}^{1+}]$

$$\text{pH} = -\log [2.4 \times 10^{-6}]$$

$$\boxed{\text{pH} = 5.62} \leftarrow \text{an acidic solution!}$$

Q2: What is the hydrogen ion concentration $[\text{H}^{1+}]$ of a solution whose pH is 4.50?

A2: $\text{pH} = -\log [\text{H}^{1+}]$

$$4.50 = -\log [\text{H}^{1+}]$$

$$\boxed{[\text{H}^{1+}] = 3.2 \times 10^{-5} \text{ M}}$$

- Sorensen also proposed the term pOH (for "power of the hydroxide ion") as a measure of a solution's hydroxide ion concentration and which equaled the negative logarithm of the hydroxide ion concentration.

Q3: What is the pOH of a solution whose $[\text{OH}^{1-}]$ concentration is $5.8 \times 10^{-3} \text{ M}$?

A3: $\text{pOH} = -\log [\text{OH}^{1-}]$

$$\text{pOH} = -\log [5.8 \times 10^{-3}]$$

$$\boxed{\text{pOH} = 2.24}$$

Q4: What is the hydroxide ion concentration $[\text{OH}^{1-}]$ of a solution whose pOH is 9.25?

A4: $\text{pOH} = -\log [\text{OH}^{1-}]$

$$9.25 = -\log [X]$$

$$\boxed{X = 5.6 \times 10^{-10} \text{ M OH}^{1-}}$$

- In aqueous solutions, **pH + pOH = 14.** $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

Q5: What is the pOH of a solution whose pH = 8.68?

A5: $\text{pOH} = 14 - \text{pH}$

$$\text{pOH} = 14 - 8.68$$

$$\boxed{\text{pOH} = 5.32}$$

Q6: What is the $[\text{OH}^{1-}]$ of a solution whose pH = 8.68?

A6: $\text{pOH} = 14 - \text{pH} = 14 - 8.68 = 5.32$

$$\text{pOH} = -\log [\text{OH}^{1-}]$$

$$5.32 = -\log [X]$$

$$\boxed{X = 4.8 \times 10^{-6} \text{ M OH}^{1-}}$$

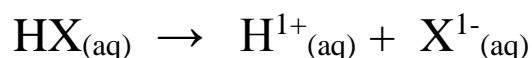
IV – Strong Acids and Strong Bases

A) Strong Acids

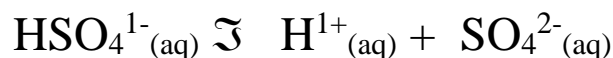
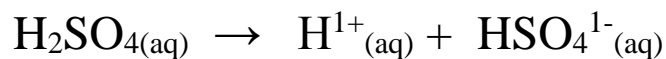
- All acids form an equilibrium between the molecular species and the ions. For strong acid, the equilibrium is **very far** to the right.



- Strong monoprotic acids are acids ionize "***completely***" in water to form hydrogen ions (H^{1+}) and anions.



- HI, HBr, HCl, HNO_3 , HClO_3 , and HClO_4 are classified as strong monoprotic acids.
- H_2SO_4 is classified as a strong diprotic acid in which the first hydrogen is completely ionized in water and the second hydrogen is partially ionized in water.



Q7: What is the pH of a 0.120 M HCl solution?

A7: Since HCl is a strong acid, then $[\text{H}^{1+}] \approx [\text{HCl}]$

$$\text{pH} = -\log [\text{H}^{1+}]$$

$$\text{pH} = -\log [0.120]$$

$$\boxed{\text{pH} = 0.921}$$

Q8: The pH of HNO_3 solution is 5.26. What is the concentration of the solution?

A8: Since HNO_3 is a strong acid, then $[\text{H}^{1+}] \approx [\text{HNO}_3]$

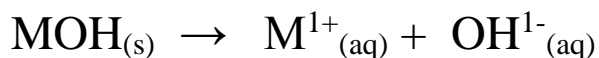
$$\text{pH} = -\log [\text{H}^{1+}]$$

$$5.26 = -\log [\text{X}]$$

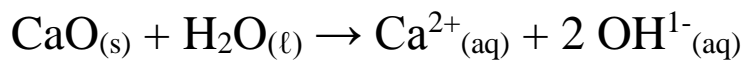
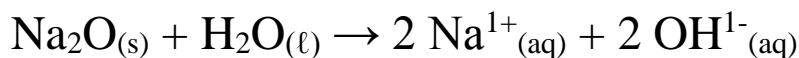
$$\text{X} = 5.5 \times 10^{-6} \text{ M } \text{H}^{1+} \rightarrow [\text{HNO}_3] = \boxed{5.5 \times 10^{-6} \text{ M}}$$

B) Strong Bases

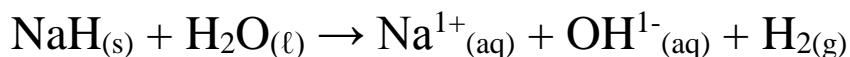
- Soluble Ionic hydroxides are strong bases which **dissociate in water** to form hydroxide ions (OH^{1-}) and metallic cations.



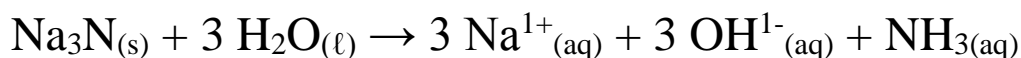
- LiOH , NaOH , KOH , RbOH , CsOH , $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$ classified as strong bases.
- $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$ have limited solubility in water – especially $\text{Ca}(\text{OH})_2$. Thus only saturated solutions of $\text{Ca}(\text{OH})_2$ will reach pH's near 14.
- Soluble metallic oxides are strong bases which **react with water** to form hydroxide ions (OH^{1-}) and metallic cations.



- Soluble metallic hydrides are strong bases which **react with water** to form hydroxide ions (OH^{1-}), metallic cations, and hydrogen gas.



- Soluble metallic nitrides are strong bases which **react with water** to form hydroxide ions (OH^{1-}), metallic cations, and ammonia.



Q9: What is the pH of a 0.00012 M $\text{Ba}(\text{OH})_2$ solution?

A9: Since $\text{Ba}(\text{OH})_2$ is a strong base, then $[\text{OH}^{1-}] = 2[\text{Ba}(\text{OH})_2]$

$$[\text{H}^{1+}] = K_w / [\text{OH}^{1-}]$$

$$\text{pH} = -\log [\text{H}^{1+}]$$

$$\text{pH} = -\log [(1.0 \times 10^{-14}) / 2(0.00012)]$$

$$\boxed{\text{pH} = 10.38}$$

$$\text{pOH} = -\log [\text{OH}^{1-}]$$

$$\text{pOH} = -\log [0.00024]$$

$$\text{pOH} = 3.62$$

$$\boxed{\text{pH} = 10.38}$$

Chapter-16

Lesson-3

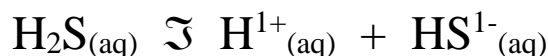
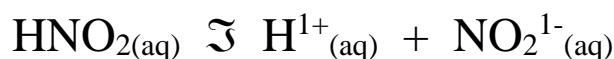
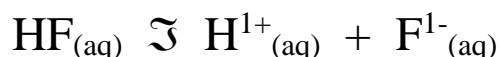
V – Weak Acids

- Weak acids are acids that only partially ionize in water to form an equilibrium between the molecular species and the ions

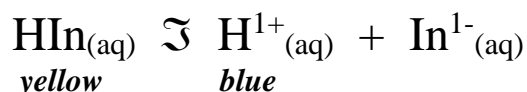


- The lower the initial concentration of the weak acid the more it will ionize [*1.00 M HF ionizes 2.6% while 0.01 M HF ionizes 26%*].
- Weak acids can be classified into three categories.

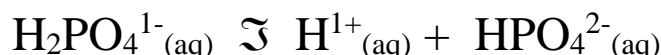
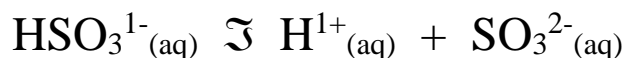
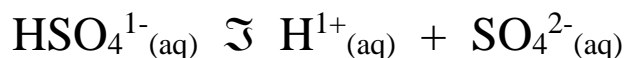
1) Molecules containing an ionizable hydrogen atom



Acid-Base indicators "HIn" are molecular weak acids.

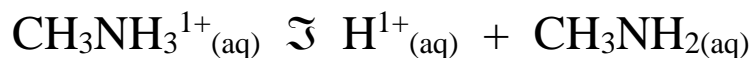
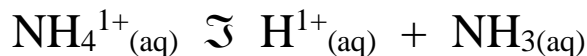


2) Anions containing a readily ionizable hydrogen ion



3) Cations

All cations act as weak acids except for group-1 metals and Ca^{2+} , Sr^{2+} , and Ba^{2+} .



Q1: You are given a 0.050M solution of a mystery acid, HX, whose pH is 3.10. (i) Calculate the $[\text{H}^{1+}]$ and the $[\text{OH}^{1-}]$ of the solution. (ii) Is the acid a strong acid or weak acid? (iii) Calculate the percent ionization of the mystery acid.

A1: (i) $\text{pH} = -\log [\text{H}^{1+}]$

$$3.10 = -\log [\text{H}^{1+}]$$

$$[\text{H}^{1+}] = 7.9 \times 10^{-4} \text{ M}$$

$$K_w = [\text{H}^{1+}][\text{OH}^{1-}]$$

$$1.0 \times 10^{-14} = [7.9 \times 10^{-4}][\text{OH}^{1-}]$$

$$[\text{OH}^{1-}] = 1.3 \times 10^{-11} \text{ M}$$

(ii) The mystery acid, HX, is a **weak acid** because it only *partially* ionizes in water.

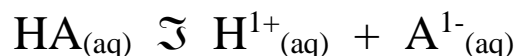
$$\text{(iii) } \frac{7.9 \times 10^{-4} \text{ M}}{0.050 \text{ M}} \times 100$$

$$1.6\% \text{ ionization}$$



A) The Equilibrium Expression (K_a) for Weak Acids

- Aqueous solutions of weak acids exist in equilibrium with their conjugate bases.



- The equilibrium expression for this weak acid is...

$$K_a = \frac{[\text{H}^{1+}][\text{A}^{1-}]}{[\text{HA}]}$$

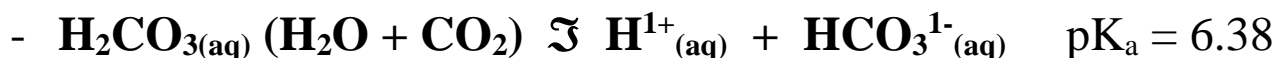
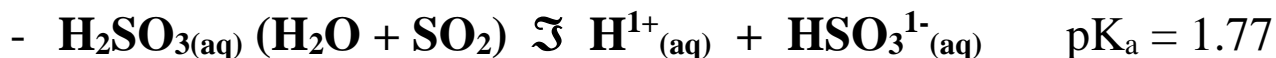
- All weak acids only partially ionize in water but some ionize to a greater extent (the "strong" weak acids) than others (the "weak" weak acids).
- the "strong" weak acids have larger K_a values and the "weak" weak acids have smaller K_a values.



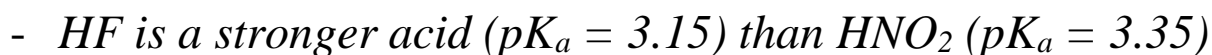
Thus H_3PO_4 is a stronger acid than HCHO_2 .

- Another measure of a weak acid's "strength" is its $\text{p}K_a$.

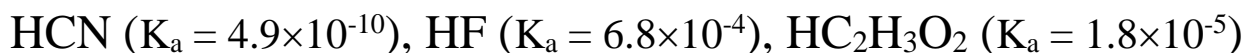
$$\text{p}K_a = -\log K_a$$



The stronger weak acid have the smaller $\text{p}K_a$ value.



Q2: Rank the following acids from strongest to weakest.



A2: HF , $\text{HC}_2\text{H}_3\text{O}_2$, HCN

B) Calculating of K_a from pH

- K_a values for all weak acids must be determined experimentally!
- The value of a weak acid's K_a can be determined from the pH of its aqueous solution.

Q3: If the pH of a 0.1000 M solution of the weak acid HClO is 4.26, then determine the K_a for HClO .



If pH = 4.26, then at equilibrium $[\text{H}^{1+}] = 5.5 \times 10^{-5} \text{ M}$.

Rx	$\text{HClO}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{ClO}^{1-}_{(\text{aq})}$
I	0.1000		0.0000		0.0000
C	$- 5.5 \times 10^{-5}$		$+ 5.5 \times 10^{-5}$		$+ 5.5 \times 10^{-5}$
E	0.0995		5.5×10^{-5}		5.5×10^{-5}

$$K_a = \frac{[\text{H}^{1+}][\text{ClO}^{1-}]}{[\text{HClO}]} \longrightarrow K_a = \frac{[5.5 \times 10^{-5}][5.5 \times 10^{-5}]}{[0.0995]}$$

$$K_a = 3.0 \times 10^{-8}$$

Q4: If the pH of a 0.0100 M solution of the weak acid $\text{HC}_4\text{H}_7\text{O}_2$ (butanoic acid) is 3.41, then determine the K_a for $\text{HC}_4\text{H}_7\text{O}_2$.



If pH = 3.41, then at equilibrium $[\text{H}^{1+}] = 0.00038 \text{ M}$.

Rx	$\text{HC}_4\text{H}_7\text{O}_{2(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{C}_4\text{H}_7\text{O}_2^{1-}_{(\text{aq})}$
I	0.0100		0.0000		0.0000
C	$- 0.00038$		$+ 0.00038$		$+ 0.00038$
E	0.0096		0.00038		0.00038

$$K_a = \frac{[\text{H}^{1+}][\text{C}_4\text{H}_7\text{O}_2^{1-}]}{[\text{HC}_4\text{H}_7\text{O}_2]} \longrightarrow K_a = \frac{[0.00038][0.00038]}{[0.0096]}$$

$$K_a = 1.5 \times 10^{-5}$$

C) Calculating of pH from K_a

- The pH of a weak acid solution can be predicted from the K_a as long as the concentration is known.

Q5: Calculate the pH of a 1.000 M solution of HF (6.8×10^{-4}).

A5: $\text{HF}_{(\text{aq})} \rightleftharpoons \text{H}^{1+}_{(\text{aq})} + \text{F}^{1-}_{(\text{aq})}$

Rx	$\text{HF}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{F}^{1-}_{(\text{aq})}$
I	1.000		0.000		0.000
C	- X		+X		+X
E	1.000-X		X		X

$$K_a = \frac{[\text{H}^{1+}][\text{F}^{1-}]}{[\text{HF}]}$$

$$6.8 \times 10^{-4} = \frac{[\text{X}]^2}{[1.000 - \text{X}]}$$

$$6.8 \times 10^{-4} = \frac{[\text{X}]^2}{[1.000]} \longrightarrow \text{X} = 0.026 \text{ M (2.6\% of 1.000 M)}$$

pH = 1.59

Q6: Calculate the pH of a 0.10 M solution of $\text{HC}_6\text{H}_7\text{O}_6$ - *ascorbic acid* - ($K_a = 8.0 \times 10^{-5}$).

A6: $\text{HC}_6\text{H}_7\text{O}_{6(\text{aq})} \rightleftharpoons \text{H}^{1+}_{(\text{aq})} + \text{C}_6\text{H}_7\text{O}_6^{1-}_{(\text{aq})}$

Rx	$\text{HC}_6\text{H}_7\text{O}_{6(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{C}_6\text{H}_7\text{O}_6^{1-}_{(\text{aq})}$
I	0.10		0.00		0.00
C	- X		+X		+X
E	0.10-X		X		X

$$K_a = \frac{[\text{H}^{1+}][\text{C}_6\text{H}_7\text{O}_6^{1-}]}{[\text{HC}_6\text{H}_7\text{O}_6]}$$

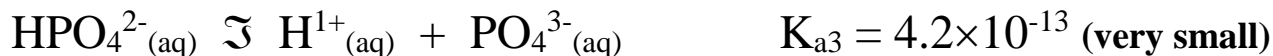
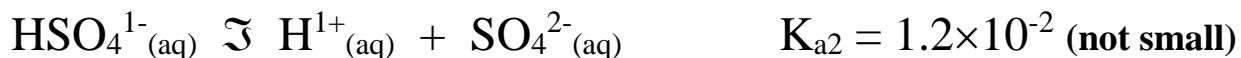
$$8.0 \times 10^{-5} = \frac{[\text{X}]^2}{[0.10 - \text{X}]}$$

$$8.0 \times 10^{-5} = \frac{[\text{X}]^2}{[0.10]} \longrightarrow \text{X} = 0.0028 \text{ M (2.8\% of 0.10 M)}$$

pH = 2.55

D) Polyprotic Acids and K_a

- Many acids have more than one ionizable hydrogen atom.



- If the K_{a1} is greater than K_{a2} by a factor of 1000 or more ***and*** if K_{a2} is small, then almost all of the H^+ is produced from the first ionization! (**Only the first ionizable hydrogen matters**)

Q7: Calculate the pH of a 1.00 M solution of H_3PO_4 .



Rx	$\text{H}_3\text{PO}_{4(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{H}_2\text{PO}_4^{1-}_{(\text{aq})}$
I	1.00		0.000		0.000
C	- X		+X		+X
E	1.00-X		X		X

$$K_{a1} = \frac{[\text{H}^{1+}][\text{H}_2\text{PO}_4^{1-}]}{[\text{H}_3\text{PO}_4]} \longrightarrow 7.5 \times 10^{-3} = \frac{[\text{X}]^2}{[1.00-\text{X}]}$$

quadratic
formula magic

$$\boxed{\text{X} = 0.083 \text{ M } \text{H}^{1+}}$$

Rx	$\text{H}_2\text{PO}_4^{1-}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{HPO}_4^{2-}_{(\text{aq})}$
I	0.083		0.083		0.000
C	- X		+X		+X
E	0.083 - X		0.083+X		X

$$K_{a2} = \frac{[\text{H}^{1+}][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^{1-}]} \quad 6.2 \times 10^{-8} = \frac{[0.083][\text{X}]}{[0.083]}$$

$$6.2 \times 10^{-8} = \frac{[0.083+\text{X}][\text{X}]}{[0.083-\text{X}]}$$

Too small
to matter!

$$\boxed{\text{X} = 6.2 \times 10^{-8} \text{ M additional } \text{H}^{1+}}$$

$$\boxed{\text{THUS pH} = 1.08}$$

Chapter-16

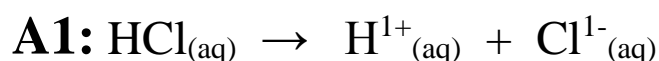
Lesson-4

VI – Comparing Strong and Weak Acid Solutions

A) Comparing Acid Solutions with Equal Concentrations

- If the concentrations are the same, a strong acid solution will always have a lower pH than a weak acid solution.

Q1: Calculate the pH of a 1.000 M solution of HCl.



$$\text{pH} = -\log [\text{H}^{1+}]$$

$$[\text{H}^{1+}] = 1.000 \text{ (100\% of 1.000 M)}$$

$$\boxed{\text{pH} = 0.00}$$

Q2: Calculate the pH of a 1.000 M solution of HF (6.8×10^{-4}).



Rx	$\text{HF}_{(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{F}^{1-}_{(\text{aq})}$
I	1.000		0.000		0.000
C	- X		+X		+X
E	1.000-X		X		X

$$\text{pH} = -\log [\text{H}^{1+}]$$

$$K_a = \frac{[\text{H}^{1+}][\text{F}^{1-}]}{[\text{HF}]}$$

$$6.8 \times 10^{-4} = \frac{[\text{X}]^2}{[1.000]}$$

$$X = 0.026 \text{ M (2.6\% of 1.000 M)}$$

$$6.8 \times 10^{-4} = \frac{[\text{X}]^2}{[1.000-X]}$$

$$\boxed{\text{pH} = 1.59}$$

B) Comparing Acid Solutions with Equal pH's

- If the pH's are the same, a strong acid solution will always have a lower concentration than a weak acid solution.

Q3: If the pH of a solution of the strong acid HNO_3 is 3.41, then determine the initial concentration of HNO_3 .



If $\text{pH} = 3.41$, then at equilibrium $[\text{H}^{1+}] = 0.00039 \text{ M}$.

Since HNO_3 is a strong acid and ionizes 100% in water, then $[\text{H}^{1+}] = [\text{HNO}_3]$

Thus...

$$[\text{HNO}_3] = 0.00039 \text{ M}$$

Q4: If the pH of a solution of the weak acid $\text{HC}_4\text{H}_7\text{O}_2$ ($K_a = 1.5 \times 10^{-5}$) is 3.41, then determine the initial concentration of $\text{HC}_4\text{H}_7\text{O}_2$.



If $\text{pH} = 3.41$, then at equilibrium $[\text{H}^{1+}] = 0.00039 \text{ M}$.

Rx	$\text{HC}_4\text{H}_7\text{O}_{2(\text{aq})}$	\rightleftharpoons	$\text{H}^{1+}_{(\text{aq})}$	+	$\text{C}_4\text{H}_7\text{O}_2^{1-}_{(\text{aq})}$
I	X		0.00000		0.00000
C	- 0.00039		+0.00039		+0.00039
E	X-0.00039		0.00039		0.00039

$$K_a = \frac{[\text{H}^{1+}][\text{C}_4\text{H}_7\text{O}_2^{1-}]}{[\text{HC}_4\text{H}_7\text{O}_2]}$$

$$1.5 \times 10^{-5} = \frac{[0.00039][0.00039]}{[X-0.00039]}$$

$$X = 0.010 \text{ M}$$

$$[\text{HC}_4\text{H}_7\text{O}_2] = 0.011 \text{ M}$$

VII – Weak Bases

- Weak bases are bases that ...
 - a) barely dissociate into cations and hydroxide ions.
 - b) produce hydroxide ions by reacting with water in water.
- Common weak bases can be classified into three categories.

1) Molecules containing a nitrogen with a lone pair of electrons

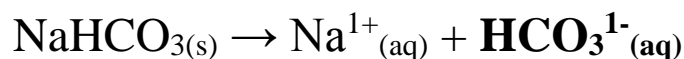
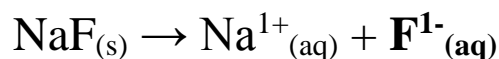
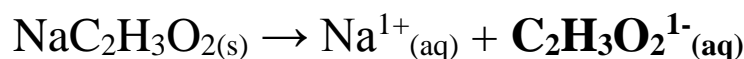
a) Ammonia



- b) Amines are organic molecular bases which have the general formula, R–NH₂, where “R” is a hydrocarbon group.



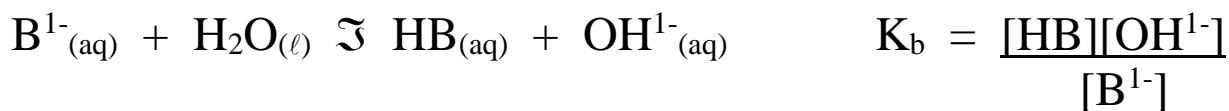
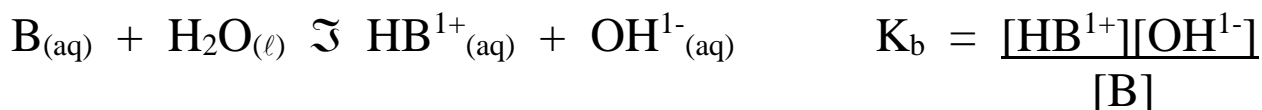
2) Anions derived from weak acids (in the form a salt)



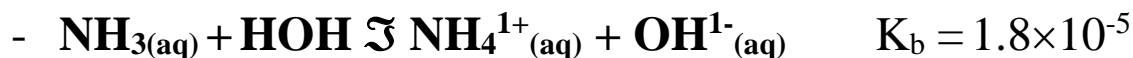
3) Insoluble Hydroxides

C) The Equilibrium Expression for K_b

- Aqueous solutions of weak bases exist in equilibrium with their conjugate acids.



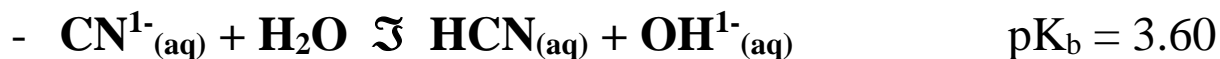
- All weak bases only partially ionize in water but some ionize to a greater extent (the "strong" weak bases) than others (the "weak" weak bases).
- the "strong" weak bases have larger K_b values and the "weak" weak bases have smaller K_b values.



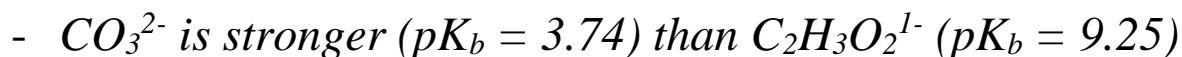
Thus NH_3 is a **stronger** base than F^{1-} (in the form of NaF, KF, ...)

- Another measure of a weak base's "strength" is its pK_b .

$$pK_b = -\log K_b$$



Thus the **stronger** the bases are the **smaller** their pK_b 's value will be.



D) pH and pOH

- The pH of a solution plus the pOH of the same solution equals 14.

$$\text{If } [H^{1+}] \times [OH^{1-}] = 1.0 \times 10^{-14}, \text{ then } pH + pOH = 14$$

E) Calculation of $[\text{OH}^{1-}]$ and pH in a Weak Base

Q5: Calculate the $[\text{OH}^{1-}]$ and the pH in a solution of 1.00 M Na_2CO_3 ($K_b = 1.8 \times 10^{-4}$).

A5: $\text{Na}_2\text{CO}_{3(\text{aq})} \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^{1-}(\text{aq}) + \text{OH}^{1-}(\text{aq})$

	CO_3^{2-}	HCO_3^{1-}	OH^{1-}
Initial (M)	1.00	0.00	0.00
Change (M)	- X	+ X	+ X
Equilibrium (M)	1.00 - X	X	X

$$K_b = \frac{[\text{HCO}_3^{1-}][\text{OH}^{1-}]}{[\text{CO}_3^{2-}]} \rightarrow 1.8 \times 10^{-4} = \frac{[X][X]}{[1.00-X]}$$

Assume $[1.00-X] \approx [1.00]$

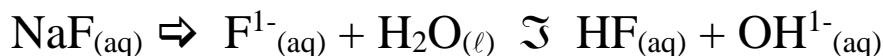
$$X = 0.013 \text{ M OH}^{1-} \quad (\text{only } 1.3\% \text{ of } 1.00 \text{ M})$$

$$\text{pOH} = 1.89 \rightarrow \text{pH} = 12.11$$

Q6: Calculate the $[\text{OH}^{1-}]$ and the **initial** number of grams of NaF added to make a 1.00L solution whose pH is 8.00. ($K_b = 1.5 \times 10^{-11}$).

A6: $\text{pH} = 8.00 \rightarrow \text{pOH} = 6.00$

$$[\text{OH}^{1-}] = 1.0 \times 10^{-6} \text{ M} \quad (0.0000010 \text{ M}) \text{ at equilibrium}$$



	F^{1-}	HF	OH^{1-}
Initial (M)	X	0.00	0.00
Change (M)	- 0.0000010	+ 0.0000010	+ 0.0000010
Equilibrium (M)	X - 0.0000010	0.0000010	0.0000010

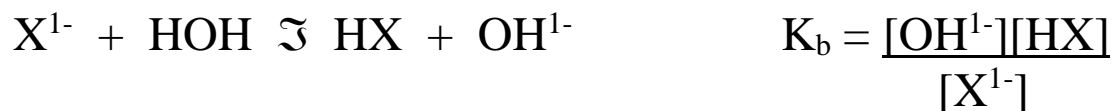
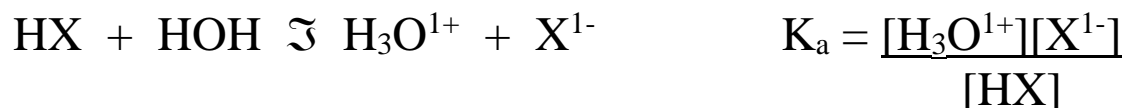
$$K_b = \frac{[\text{HF}][\text{OH}^{1-}]}{[\text{F}^{1-}]} \rightarrow 1.5 \times 10^{-11} = \frac{[0.0000010][0.0000010]}{[X - 0.0000010]}$$

$$X = 6.7 \times 10^{-2} \text{ M F}^{1-} \dots \rightarrow \mathbf{6.7 \times 10^{-2} \text{ moles NaF}} \text{ in } 1.00 \text{ L solution}$$

$$6.7 \times 10^{-2} \text{ moles} \times \frac{42.0 \text{ g}}{1 \text{ mole}} = 2.8 \text{ g NaF}$$

VIII – The Relationship between K_a and K_b

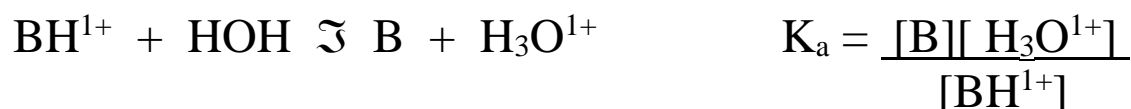
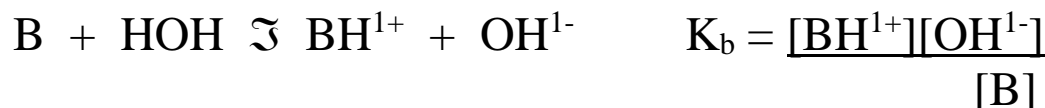
- Consider the weak acid HX and its conjugate base X^{1-} .



- The product of K_a and K_b would equal...

$$\frac{[\text{H}_3\text{O}^{1+}][\cancel{\text{X}^{1-}}]}{[\cancel{\text{HX}}]} \times \frac{[\text{OH}^{1-}][\cancel{\text{HX}}]}{[\cancel{\text{X}^{1-}}]} = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}] = K_w$$

- Consider the weak base B and its conjugate acid BH^{1+} .



- The product of K_a and K_b would equal...

$$\frac{[\cancel{\text{BH}^{1+}}][\text{OH}^{1-}]}{[\text{B}]} \times \frac{[\text{B}][\text{H}_3\text{O}^{1+}]}{[\cancel{\text{BH}^{1+}}]} = [\text{OH}^{1-}][\text{H}_3\text{O}^{1+}] = K_w$$

- Since $[\text{H}^{1+}][\text{OH}^{1-}] = K_w = 1.0 \times 10^{-14}$...

$$\text{then } K_a \times K_b = K_w \quad \text{and} \quad K_w = 1.0 \times 10^{-14}$$

- Thus for conjugate acid-base pairs...

$$K_a = K_w/K_b \quad \text{and} \quad K_b = K_w/K_a$$

Q7: The K_b of the base, pyridine ($\text{C}_5\text{H}_5\text{N}$), is 4.2×10^{-8} .

Calculate the K_a of the pyridinium ion, $\text{C}_5\text{H}_5\text{NH}^{1+}$.

A7: $K_a = K_w/K_b$

$$K_a = (1.0 \times 10^{-14}) / (4.2 \times 10^{-8}) = \boxed{2.4 \times 10^{-7}}$$

Q8: The K_a of hydrofluoric acid (HF) is 6.8×10^{-4} .

Calculate the K_b of the fluoride ion, F^{1-} .

A8: $K_b = K_w/K_a$

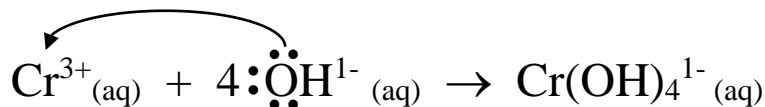
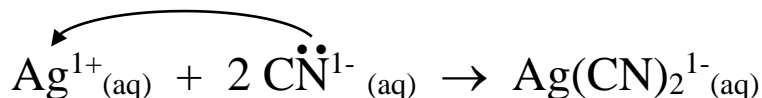
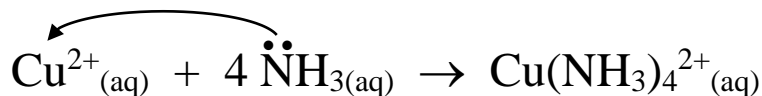
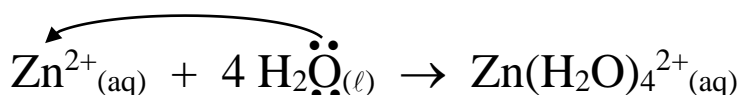
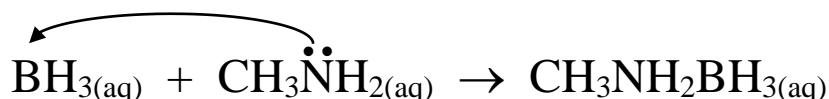
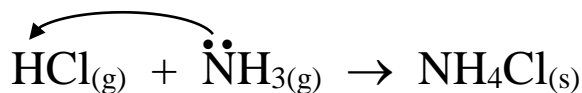
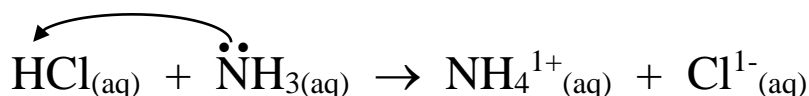
$$K_b = (1.0 \times 10^{-14}) / (6.8 \times 10^{-4}) = \boxed{1.5 \times 10^{-11}}$$

Chapter-16

Lesson-5

IX – Lewis Acids and Bases

- A **Lewis acid** is a substance that accepts an electron pair during a reaction.
- A **Lewis base** is a substance that donates an electron pair during a reaction. A **Lewis base** must have a lone electron pair to donate.



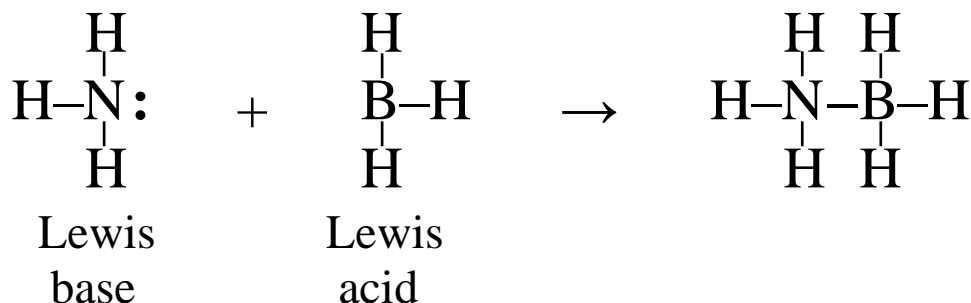
Q1: Identify the Lewis acid and Lewis base among the reactants:



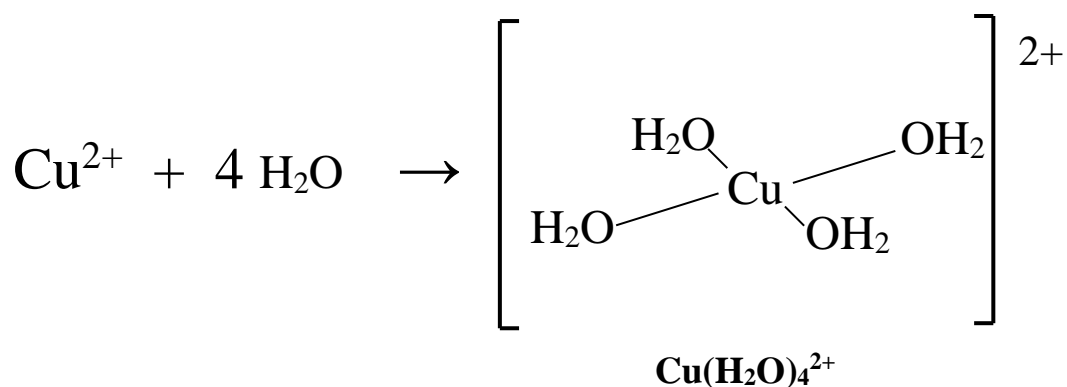
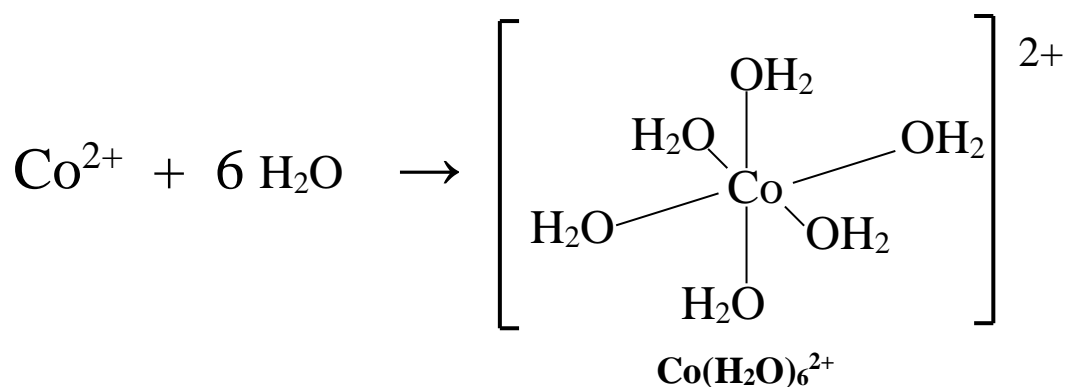
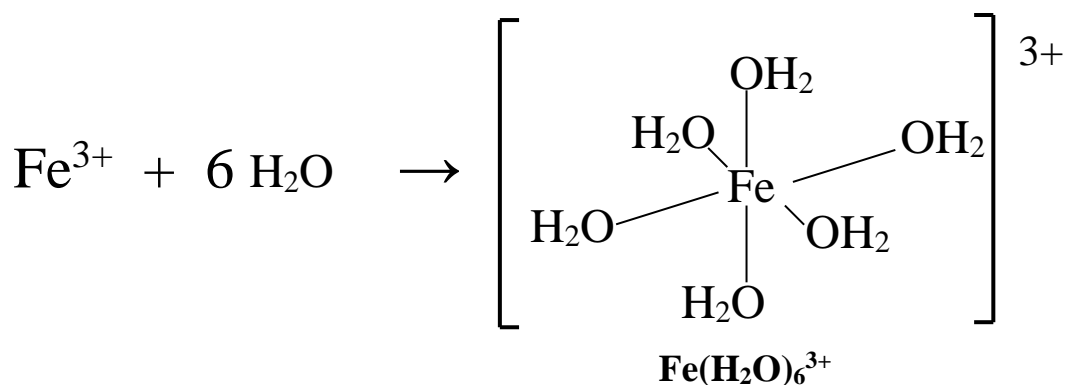
A1: (i) Lewis acid: $\text{Fe}(\text{ClO}_4)_3$ or Fe^{3+} Lewis base: H_2O

(ii) Lewis acid: BF_3 Lewis base: $(\text{CH}_3)_3\text{N}$

- In all Lewis acid-base reactions a species is produced that possesses a new covalent bond (a coordinate covalent bond).

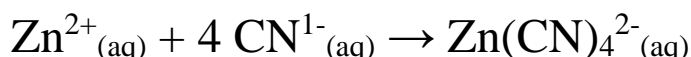
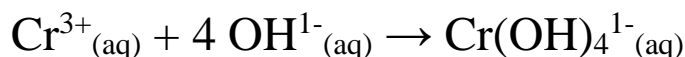
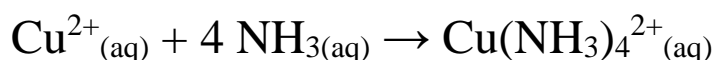
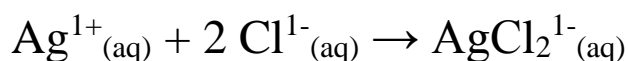
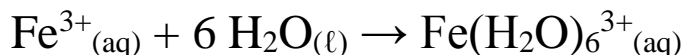


- The process of the hydration of a metallic cation in water can be thought of a Lewis acid-base reaction where the water molecules are the Lewis bases and the metallic cation is the Lewis acid.

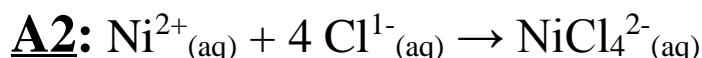


X –Complex Ions

- An ion containing a central metallic cation to which two or more Lewis bases are attached by coordinate covalent bonds is called a **complex ion**.
- The most common complex ions are those formed by cations of aluminum or the transition metals, Cr, Fe, Co, Ni, Cu, Zn, & Ag.
- The most common complex ions are those formed by the Lewis bases, Cl^{1-} , OH^{1-} , H_2O , NH_3 , & CN^{1-} .
- The total charge of a complex ion is equal to the total sum of the charges of the metallic cation and the Lewis bases present.



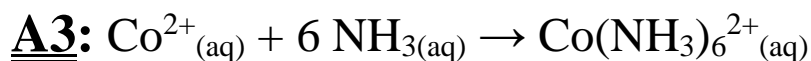
Q2: Write the balance equation for the formation of the complex ion of a nickel II ion and four chloride ions and then identify the Lewis acid and Lewis base in the reaction.



Lewis acid: Ni^{2+}

Lewis base: Cl^{1-}

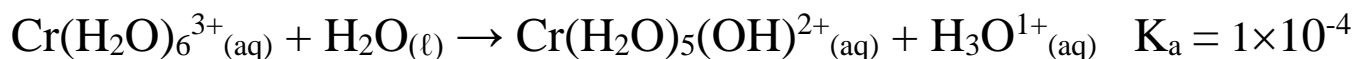
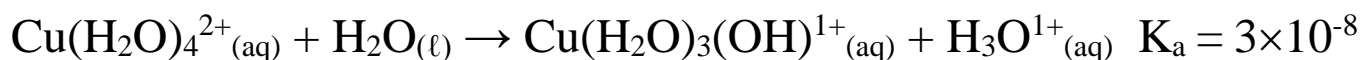
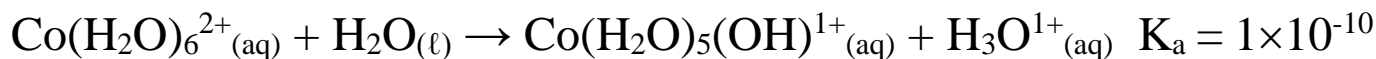
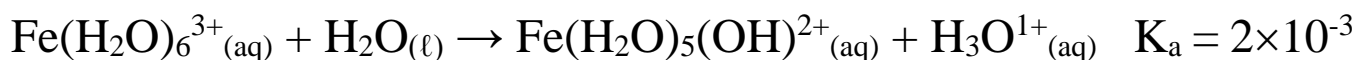
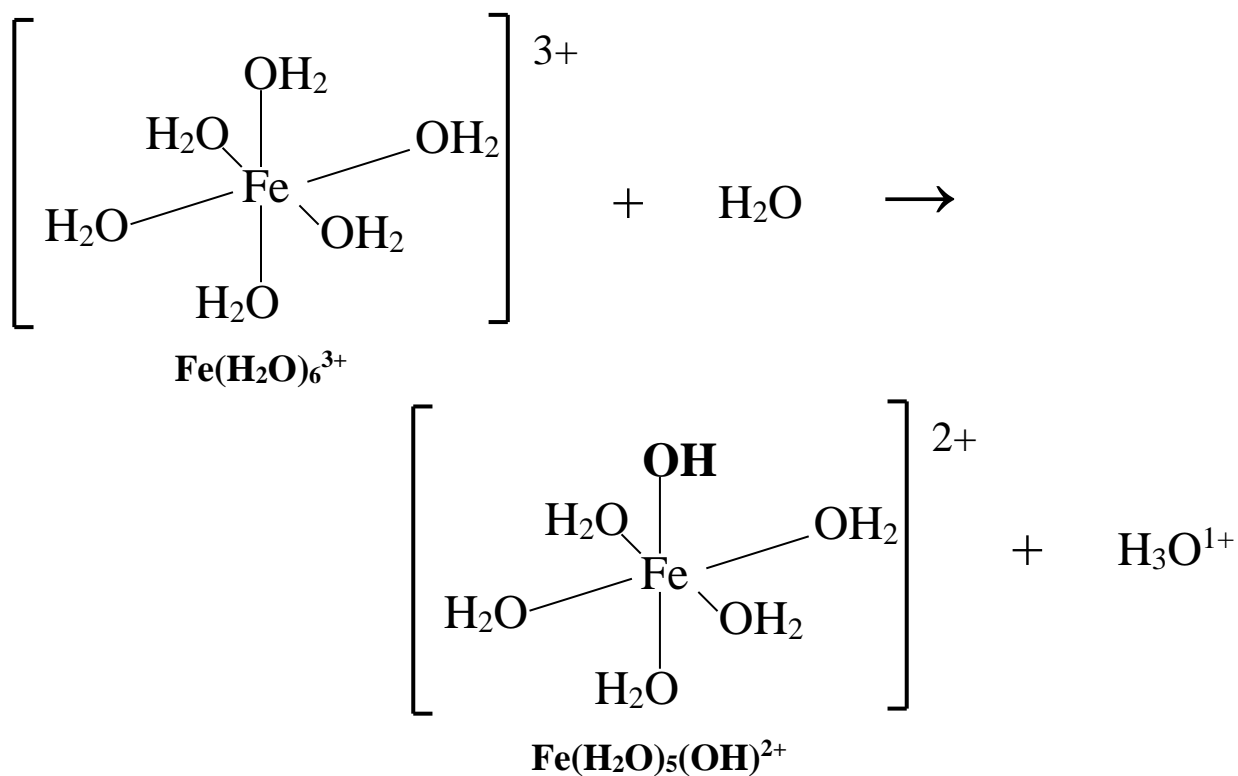
Q3: Write the balance equation for the formation of the complex ion of a cobalt II ion and six ammonia molecules and then identify the Lewis acid and Lewis base in the reaction.



Lewis acid: Co^{2+}

Lewis base: NH_3

- **Remember**, hydrated metallic cations are weak acids.
- Hydrated metallic cations are complex ions which slightly ionize in water. This occurs when the hydrated metallic cation donates a hydrogen atom from one of its bonded water molecules to one of the free water molecules in the solution.



Q4: Which of the following hydrated metallic cations behaves as the strongest acid in water?

$\text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq})$, $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq})$, $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq})$, or $\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq})$

A4: $\text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ because it has the largest K_a value. (Smaller and more highly charged cations make stronger Lewis acids.)

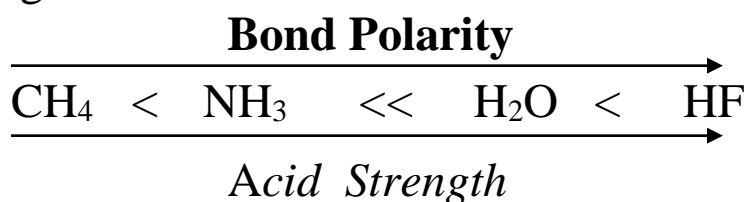
Chapter-16

Lesson-6

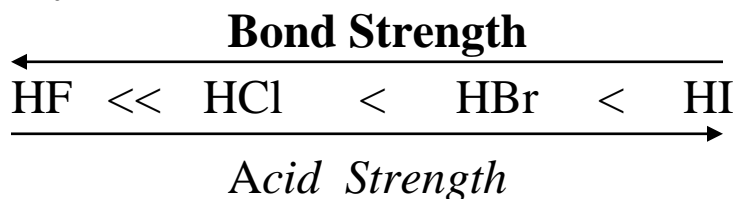
XI – Acid-Base Character and Chemical Structure

A) Factors Affecting Binary Acid Strength

- The strength of an acid often a combination of three factors:
 - 1) The polarity of the H–X bond. [when in the same period]
The more polar the bond [$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{X}}$], the stronger the acid.
 - 2) The strength of the H–X bond. [when in the same group]
The weaker the H–X bond, the stronger the acid.
 - 3) The stability of the conjugate base X^{1-} .
The more stable the conjugate base [X^{1-}], the stronger the acid.
- The strength of binary acids from the same period is mostly determined by the **bond polarity** and to a lesser extent by the bond strength:



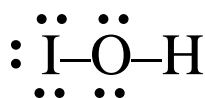
- The strength of binary acids from the same group is mostly determined by the **bond strength** and to a lesser extent by the bond polarity:



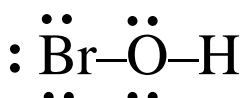
Notice that HF has a greater bond polarity than HI, but that I^{1-} is a more stable conjugate base than F^{1-} .

B) Factors Affecting Oxyacid Strength

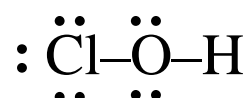
- An **oxyacid** is an acid with one or more O–H groups attached to a nonmetallic central atom that may or may not also contain additional oxygen atoms attached to the same central atom.
- The more electronegative the halogen is the weaker the O–H bond is and, the stronger the acid. The higher electronegativity shifts the electron density farther from the hydrogen atom which further destabilizes the O–H bond making the hydrogen atom more ionizable.



HIO
EN_I = 2.5



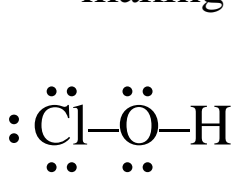
HBrO
EN_{Br} = 2.8



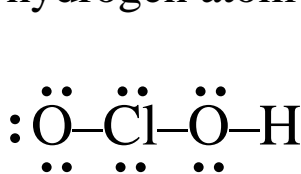
HClO
EN_{Cl} = 3.0

→
Acid Strength

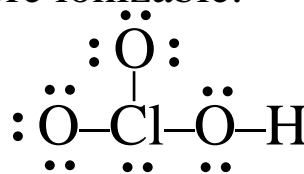
- The more oxygen atoms that surround the central atom the weaker the O–H bond is and, the stronger the acid. The highly electronegative oxygen atoms shift the electron density farther from the hydrogen atom which further destabilizes the O–H bond making the hydrogen atom more ionizable.



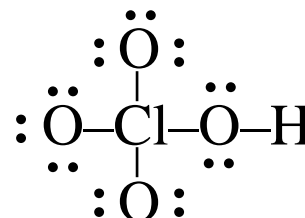
HClO



HClO₂



HClO₃

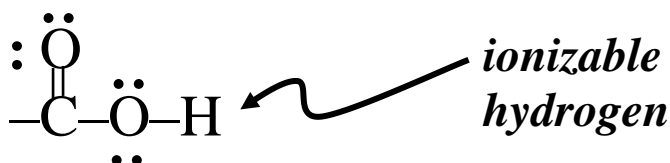


HClO₄

→
Acid Strength

C) Factors Affecting Carboxylic Acid Strength

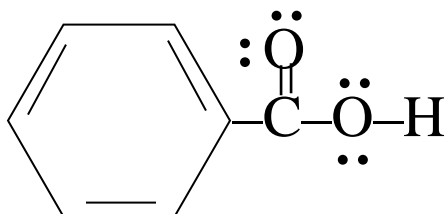
- A **carboxylic acid** is an acid that contains a carboxyl group. Only the hydrogen attached to the carboxyl group is ionizable.



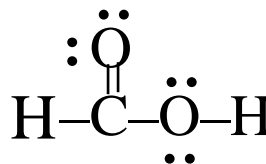
- The **carboxylate anion** exhibits resonance which increases its stability by spreading out the negative charge over several atoms making it a less capable proton acceptor.



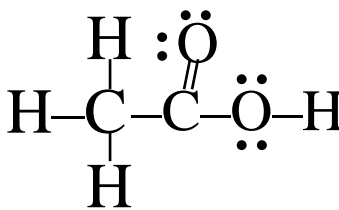
- The **carboxyl group** is attached to different “R-groups”



benzoic acid
 $K_a = 6.3 \times 10^{-5}$

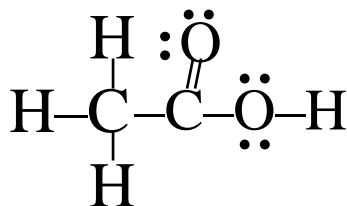


formic acid
 $K_a = 1.8 \times 10^{-4}$

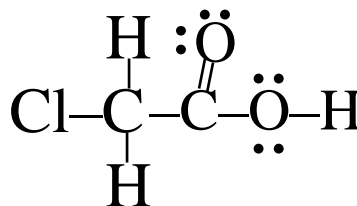


acetic acid
 $K_a = 1.8 \times 10^{-5}$

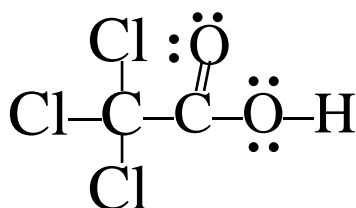
- A **carboxylic acid's** strength increases as more electronegative elements are substituted.



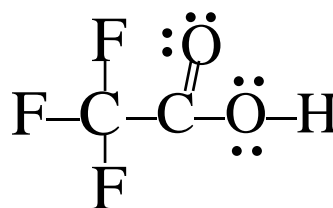
acetic acid
 $K_a = 1.8 \times 10^{-5}$



chloroacetic acid
 $K_a = 1.4 \times 10^{-3}$



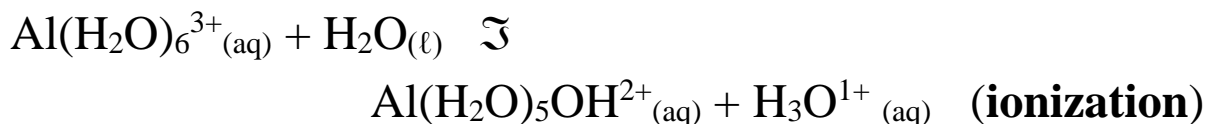
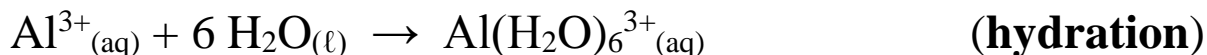
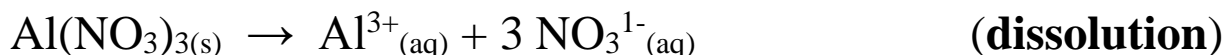
trichloroacetic acid
 $K_a = 3.0 \times 10^{-1}$



trifluoroacetic acid
 $K_a = 5.0 \times 10^{-1}$

D) Factors Affecting Hydrated Metallic Cation Strength

- A **hydrated metallic cation** can act as an acid because one of the water molecules surrounding the cation can donate a proton.



- The more highly charged the more acidic the metallic ions will be in water. For metallic ions with the same charge, the more electronegative the more acidic the metallic ions will be in water.



$$\text{K}_a = 2 \times 10^{-3}$$

$$\text{EN} = 1.8$$



$$\text{K}_a = 1 \times 10^{-4}$$

$$\text{EN} = 1.6$$



$$\text{K}_a = 1 \times 10^{-9}$$

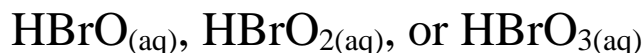
$$\text{EN} = 1.6$$



$$\text{K}_a = 1 \times 10^{-10}$$

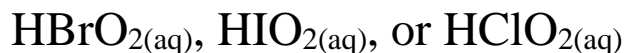
$$\text{EN} = 1.9$$

Q1: Which of the following is the strongest acid in water?



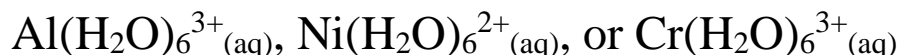
A1: HBrO_3 because the central bromine is surrounded by the most oxygen atoms.

Q2: Which of the following is the strongest acid in water?



A2: $\text{HClO}_2(\text{aq})$ because the central chlorine is the most electronegative.

Q3: Which of the following is the weakest acid in water?



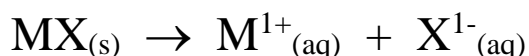
A3: $\text{Cu}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ because it has the smallest charge.

Chapter-16

Lesson-7

XII – Acid-Base Properties of Salts

- A salt is an ionic compound containing a cation other than H^{1+} and an anion other than OH^{1-} .
- When a salt dissolves in water, the ions dissociate.



- Salts can be classified as **soluble** or **insoluble**.
- Salts can also be classified as **acidic**, **basic**, or **neutral**. The effect of the cations and anions must be separately considered in order to classify a salt as acidic, basic, or neutral.

A) Neutral Salts

- Neutral salts are salts formed from a strong acid and a strong base.

- NaCl	<u>HCl</u> [acid]	<u>NaOH</u> [base]
- K ₂ SO ₄	<u>H₂SO₄</u> [acid]	<u>KOH</u> [base]
- CaBr ₂	<u>HBr</u> [acid]	<u>Ca(OH)₂</u> [base]
- Sr(NO ₃) ₂	<u>HNO₃</u> [acid]	<u>Sr(OH)₂</u> [base]
- Ba(ClO ₃) ₂	<u>HClO₃</u> [acid]	<u>Ba(OH)₂</u> [base]

B) Basic Salts

- Basic salts are salts formed from a weak acid and a strong base.

- KF	<u>HF</u> [acid]	<u>KOH</u> [base]
- Na ₂ CO ₃	<u>H₂CO₃</u> [acid]	<u>NaOH</u> [base]
- Ba(C ₂ H ₃ O ₂) ₂	<u>HC₂H₃O₂</u> [acid]	<u>Ba(OH)₂</u> [base]
- Sr ₃ (PO ₄) ₂	<u>H₃PO₄</u> [acid]	<u>Sr(OH)₂</u> [base]
- LiNO ₂	<u>HNO₂</u> [acid]	<u>LiOH</u> [base]

C) Acidic Salts

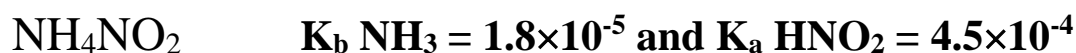
- Acidic salts are salts formed from a strong acid and a weak base.

- MgSO_4	<u>H_2SO_4</u> [acid]	<u>$\text{Mg}(\text{OH})_2$</u> [base]
- $\text{Cu}(\text{NO}_3)_2$	<u>HNO_3</u> [acid]	<u>$\text{Cu}(\text{OH})_2$</u> [base]
- NH_4Cl	<u>HCl</u> [acid]	<u>NH_3</u> [base]
- $\text{CH}_3\text{NH}_3\text{Br}$	<u>HBr</u> [acid]	<u>CH_3NH_2</u> [base]

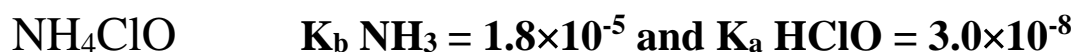
D) Salts of Weak Acid and Weak Bases

- Salts, formed from a weak acid and a weak base, are more difficult to categorize on sight. They may be acid, basic, or neutral depending on the value of the K_a of the acid and the K_b of the base.

- If the $K_a > K_b$ then the salt is acidic.



- If the $K_a < K_b$ then the salt is basic.



- If the $K_a = K_b$ then the salt is neutral.



Exceptions:

The anions HSO_4^{1-} , HSO_3^{1-} and $\text{H}_2\text{PO}_4^{1-}$ produce large enough hydrogen ion concentrations in water to classify their salts as acidic:

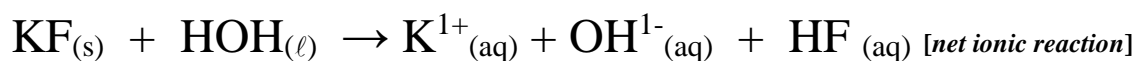
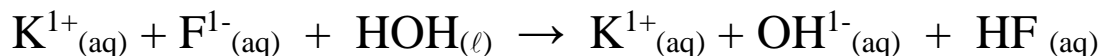
- KHSO_4	<u>H_2SO_4</u> [acid]	<u>KOH</u> [base]
- NaHSO_3	<u>H_2SO_3</u> [acid]	<u>NaOH</u> [base]
- NaH_2PO_4	<u>H_3PO_4</u> [acid]	<u>NaOH</u> [base]

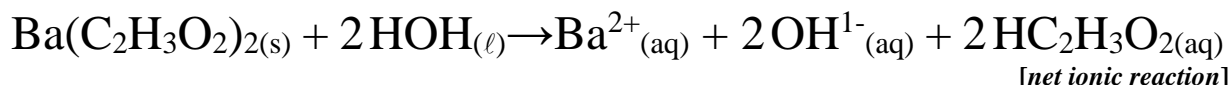
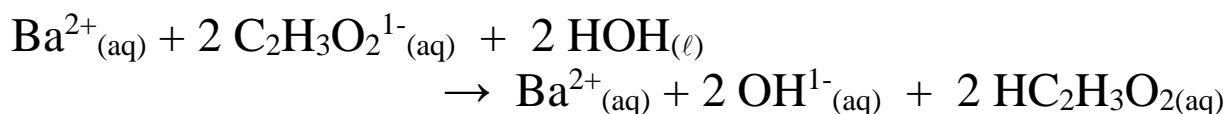
Hydrated metallic cations with 3+ charges and weak acid anions produce large enough hydrogen ion concentrations in water to classify their salts as acidic:

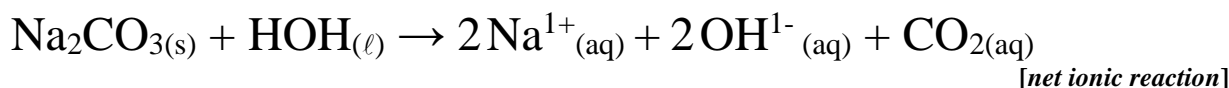
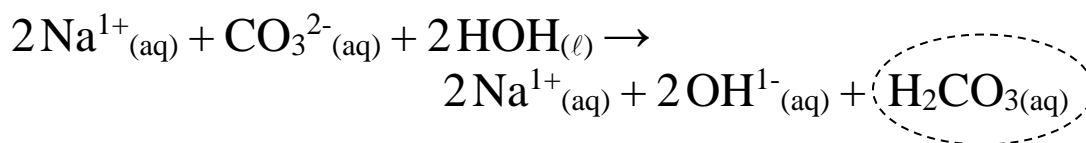
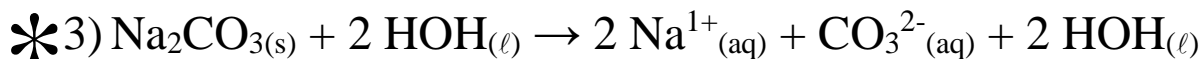
- $\text{Fe}_2(\text{SO}_3)_3$	<u>H_2SO_3</u> [acid]	<u>$\text{Fe}(\text{OH})_3$</u> [base]
- $\text{Cr}(\text{CN})_3$	<u>HCN</u> [acid]	<u>$\text{Cr}(\text{OH})_3$</u> [base]
- $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$	<u>$\text{HC}_2\text{H}_3\text{O}_2$</u> [acid]	<u>$\text{Al}(\text{OH})_3$</u> [base]

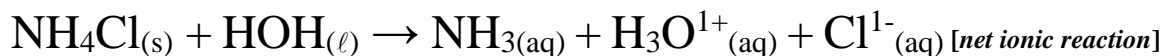
E) Hydrolysis Reactions of Salts in Water

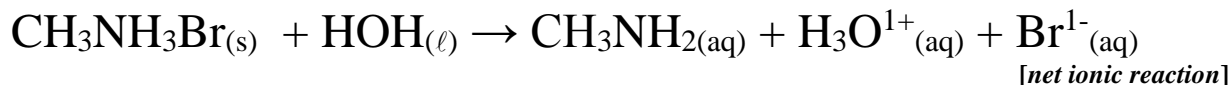
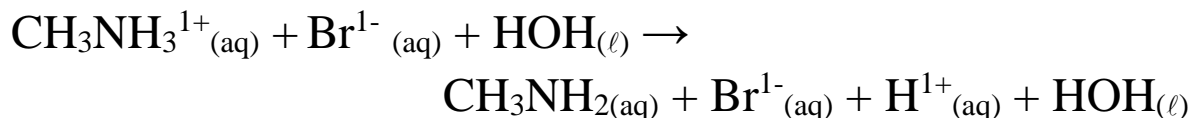
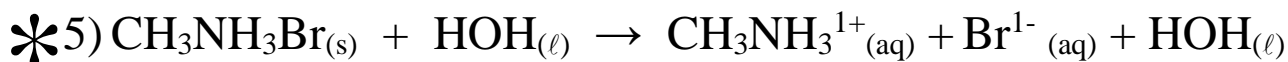
- A reaction in which a compound chemically reacts with water is called **hydrolysis**.
- Except those salts formed from a strong acid and a strong base, all other salts **hydrolyze** with the water as they dissolve in the water.



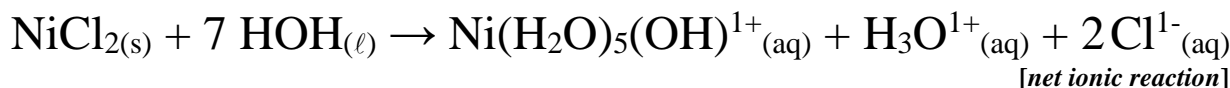
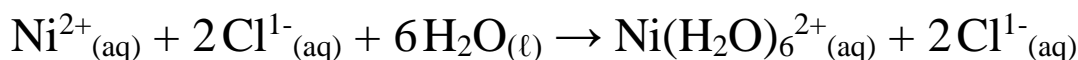


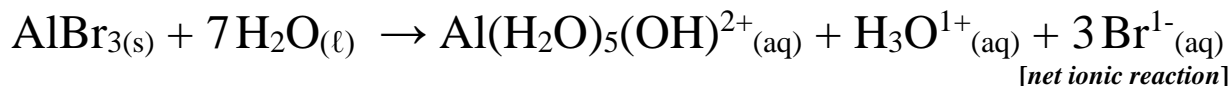
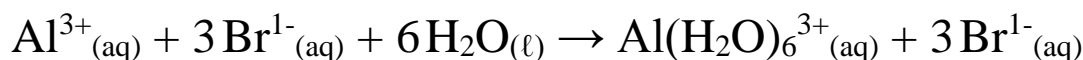






- All metal ions hydrolyze in water. [*except for group-1 and lower group-2*]





- Insoluble hydrated metallic hydroxides are able to dissolve in acid solutions.

